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"An Investigation of Solar Wind Effects on the Evolution of the Martian Atmosphere"

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This investigation concentrated on the question of how atmosphere escape, related to both photochemistry and the Mars solar wind interaction, may have affected the evolution of Mars' atmosphere over time. The Principal Investigator and postdoctoral researcher Martina Zhang adopted the premise that contemporary escape processes have dominated the losses to space over the past 3.5 billion years, but that the associated loss rates have been modified by solar evolution. A model was constructed for the contemporary escape scenario based on knowledge gained from both Venus in-situ measurements from Pioneer Venus Orbiter and Mars measurements from Phobos-2. Venus provided a valuable second example of a weakly magnetized planet having a similar solar wind interaction where we have more knowledge from observations. The model included photochemical losses from recombining ionospheric molecular ions, scavenging of Martian upper atmosphere ("pickup") ions by the solar wind, and sputtering of the atmosphere by reentering pickup ions. The existence of the latter mechanism was realized during the course of the supported investigation, and is now thought by Jakosky and Pepin (personal communication) to explain some of the Martian noble gas isotope ratios.

Our models incorporated a history of the solar EUV flux based on stellar observations and a model of the solar wind evolution. We computed both the photochemical and solar wind-induced loss rates for the element oxygen, including sputtering, and the sputtering loss rates of CO<sub>2</sub> at three epochs: the present, 2 Gyr age, and 1 Gyr age. We collaborated with S. Bougher of the University of Arizona in order to obtain the appropriate thermospheric and ionospheric models for the prevailing EUV levels, with A. F. Nagy of the University of Michigan to obtain well-established code for modeling the exospheres, and with R. E. Johnson of the University of Virginia to ensure accuracy in our treatment of the sputtering losses.

Our models suggest that oxygen escape from Mars, from 3.5 Gyr ago to the present, accounts (conservatively) for that in about 30 m (global depth) of water. The cumulative CO<sub>2</sub> escape by sputtering was ~ 150 mb. It is considered that these estimates are conservative and may easily err by up to an order of magnitude. Considering that geophysical evidence points to a past atmosphere of ~ 0.5 - 1 bar of CO<sub>2</sub>, and surface water of up to 100s of meters equivalent global depth, our numbers for escape are significant. Jakosky (personal communication) is now using the available isotopic data, together with arguments concerning the stability of CO<sub>2</sub> ice in the deep polar caps, to reconcile these effectively unavoidable losses with other evidence on the remaining volatile inventory at Mars.

During the course of the MSATT Program the Principal Investigator and B. Jakosky of the University of Colorado co-convened an MSATT Workshop on the Evolution of the Martian Atmosphere, held in Kona, Hawaii on June 29-July 1, 1992. The Principal Investigator was also a member of the MSATT Steering Group throughout the Program, and participated in both the kickoff and final MSATT Conferences.

No patents or inventions resulted from this effort.

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M.H.G. Zhang, J. G. Luhmann, S. W. bougher and A. F. Nagy, The ancient oxygen exosphere of Mars: Implications for atmospheric evolution, *J. Geophys. Res.*, 98, 10,915-10,923, 1993.

# The Ancient Oxygen Exosphere of Mars: Implications for Atmosphere Evolution

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The evolution of the Martian atmosphere, particularly with regard to water, is influenced by (1) "nonthermal" escape of oxygen atoms created by dissociative recombination and (2) by oxygen ion pickup by the solar wind. Both processes depend on the intensity of solar EUV radiation, which affects atmosphere temperatures (scale heights) and photoionization rates, and thereby the exosphere and the fluxes of escaping atoms and ions. This study involves the calculation, by the two-stream model method of Nagy and Cravens (1988), of the exospheric hot oxygen densities for "ancient" atmospheres and ionospheres (e.g., for different EUV fluxes), and the associated neutral escape fluxes. The ion production rates above nominal ionopause altitudes are also computed and are considered to be the upper limits to losses by direct solar wind pickup. Since we do not consider the pickup ion precipitation and additional neutral escape due to the sputtering process described by Luhmann and Kozyra (1991), the results presented here represent conservative estimates of the neutral escape fluxes, but somewhat generous estimates of ion loss rates. We find that when the inferred increased solar EUV fluxes of the past are taken into account, oxygen equivalent to that in several tens of meters of water, planet-wide, should have escaped to space over the last 3 Gyr.

## INTRODUCTION

The planets are thought to have formed  $\sim 4.5 \times 10^9$  years (4.5 Gyr) ago from three components of the solar nebula [Greenberg, 1989]: rocky solids (including iron), icy solids (water, ammonia and methane) and nebular gas (predominantly hydrogen and helium). The terrestrial planets grew by accretion of rocky planetesimals in the inner solar system and their early atmospheres formed by subsequent outgassing. The removal of these (probably  $H_2$ -rich) primitive atmospheres took place in the first billion years.

One process considered important for removing the primitive atmospheres is hydrodynamic escape or "blowoff" (see Hunten *et al.* [1989] and references therein) which is important for an atmosphere of low mean molecular weight (e.g., large amounts of hydrogen). An enhanced solar EUV flux is required to drive this process. At the time of planet formation, the EUV intensity of the Sun was higher by orders of magnitude according to studies by Zahnle and Walker [1982] and others. "Impact erosion" [see Walker, 1986;

Melosh and Vickery, 1989] is another process which could have played an important role in removing the early atmospheres. Impact of a planetesimal can lead to significant loss of a planetary atmosphere if sufficient energy is imparted to the atmospheric gas to eject it from the gravitational field of the planet. Both of these loss processes act more efficiently on Mars than on the Earth and Venus because of Mars' lower gravity.

The secondary or contemporary atmospheres of the terrestrial planets are considered to have been supplied by later ( $t > 1$  Gyr) outgassing of volatile materials from the planetary interior, although late impact accretion may also have occurred [e.g., Chyba, 1990]. Outgassing occurs throughout the life of the planet. These contemporary atmospheres are lost due to escape to space or absorption by the surface. In this study we investigate this later escape from Mars to space through time of a particular element, oxygen. Oxygen is of special interest because its rate of loss is sometimes considered to control the rate of loss of water [e.g., McElroy *et al.*, 1977; Liu and Donahue, 1976].

The contemporary mechanisms for escape to space can be divided into two classes: thermal and nonthermal. In the thermal or Jeans escape process [e.g., Chamberlain and Hunten, 1987], the loss of gas from a planet is powered by the thermal energy of the gas. The thermal energy of the escaping particle must exceed its potential energy in the gravitational field of the planet. Thus, light constituents such as hydrogen and helium more easily escape from planets by thermal escape than heavier elements such as oxygen. Nonthermal escape processes include both the escape of atoms due to dissociative recombination [e.g., Fox and Dalgarno, 1983] and ion pickup by the solar wind [e.g., Luhmann, 1990]. Dissociative recombination imparts extra energy to atoms, in some cases leaving them with upward-directed velocities in excess of the escape velocity, while ion pickup by

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EVOLUTIONARY IMPACT OF SPUTTERING OF THE MARTIAN ATMOSPHERE BY  $O^+$  PICKUP IONSJ. G. Luhmann<sup>1</sup>, R. E. Johnson<sup>2</sup>, M.H.G. Zhang<sup>3</sup>

**Abstract.** Nonthermal processes such as dissociative recombination of ionospheric molecules are known to lead to loss of atmospheric constituents (N, O, C) at Mars where the gravitational potential is easily overcome by the energy imparted to the product atoms. Moreover, observations of escaping planetary ions on the PHOBOS-2 spacecraft showed that the solar wind is presently scavenging significant amounts of both oxygen and molecular species as it flows past the planet. Because both the sun and the atmosphere of Mars have changed over time, the evolutionary importance of these processes cannot be estimated by simply multiplying the contemporary loss rates by the solar system age. Models of these loss mechanisms must include consideration of the evolution of the solar EUV intensity and solar wind and their effects. Here we describe calculations of solar wind-induced loss rates for evolving solar and atmospheric conditions like those described by Zhang et al. [1992a], but including sputtering of the Martian atmosphere by reentering  $O^+$  pickup ions. The inclusion of the sputter loss increases by about 30% the cumulative, estimated loss of oxygen to that in  $\sim 50$  m of water (global surface depth) over the last  $\sim 3.5$  billion years, when contemporary loss mechanisms are thought to have become dominant. More significant is the result that these ions also sputter  $CO_2$  and its fragments in substantial amounts. That integrated loss is equivalent to  $\sim 0.14$  bar atmospheric  $CO_2$  pressure, of the order of some estimates of Mars' early atmospheric inventory.

## Introduction

Mars is thought to have had both substantial amounts of surface water and a much thicker atmosphere  $\sim 3.5$  billion years ago [e.g., see McKay and Stoker, 1989 and references therein]. Estimations of the planet's "inventory" at this time place the pressure of the early atmosphere at  $\sim 0.1$  bar or more (compared to the present  $\sim 7$  mb) and include a planet-wide equivalent "ocean" of liquid water of a few meters to a km depth. The evolution of the now thin atmosphere is thought to have proceeded by some combination of escape to space and surface adsorption. The amounts of water ice and carbonate that remain on Mars will be determined to some extent by Mars Observer [e.g., see Feldman and Jakosky, 1991], but the amount that has escaped to space in the past must be determined by modeling the escape processes over time. This requires that one take into account all significant escape processes adjusted for the evolving sun and atmosphere.

Several important atmospheric constituents at Mars, namely N, O, and C, are known to undergo nonthermal escape to space due to dissociative recombination of  $N_2^+$ ,  $O_2^+$  and  $CO^+$ , respectively, in the ionosphere [McElroy, 1974; McElroy et al., 1977; Fox and Dalgarno, 1983]. This photochemical process can impart sufficient energy to the product atoms that they escape the planet's gravitational

field (the required escape velocity at Mars is  $\sim 5$  km/s or  $\sim 0.125$  eV/amu). The resulting neutral escape fluxes can be calculated from models that require knowledge of the atmospheric density and composition, and of the ionizing EUV flux of the sun.

Atomic oxygen is the major heavy constituent of the Martian exosphere according to current models [e.g. Nagy and Cravens, 1988; Nagy et al., 1990; Ip, 1990]. This oxygen "corona" is a direct consequence of the dissociative recombination process in Mars' mainly  $O_2^+$  ionosphere [see McElroy et al., 1977]. The resulting "hot" oxygen atoms can be lost if they are moving upward and have energies in excess of  $\sim 2$  eV. In addition, the much greater number of hot atoms that are left behind to populate the exosphere can be ionized by a variety of mechanisms including photoionization by solar EUV, charge exchange with solar wind protons, and impact ionization by solar wind electrons. The oxygen ions produced in the corona can be picked up by the solar wind electric field and removed from Mars [e.g., see Luhmann, 1990], or they can reenter the atmosphere where they can sputter neutrals from the region near the exobase [see Luhmann and Kozyra, 1991]. Note that there is a distinction between sputtering by solar wind protons and helium ions [Watson et al., 1980], which is assumed negligible here, and sputtering by the heavy reentering pickup ions. The pickup ions do not suffer from the same degree of deflection because of their large gyroradii and they are more efficient sputtering agents than protons and helium ions [Johnson, 1990]. These three loss processes are coupled by their relationship to the generation of the hot O corona and their various connections to the solar EUV flux.

Energetic ion observations recently obtained on the PHOBOS-2 spacecraft [e.g. Lundin et al., 1990; Verigin et al., 1991] have inspired quantitative estimates of the net loss of atmospheric constituents by solar wind scavenging. Some of these calculations invoke momentum conservation arguments [e.g. Perez-de-Tejada, 1989; Lundin et al., 1991] which are based on the assumption that the planetary obstacle has a particular cross section to the incident solar wind within which it extracts the incident momentum. One of the difficulties with such approaches is the lack of constraints concerning both the efficiency of the momentum transfer and the size of the region of transfer. Another is the lack of specificity regarding the physics involved, which makes it difficult to evaluate the effects of the process through the history of the solar system. Our current understanding of solar wind interactions with the atmospheres of the weakly magnetized planets [e.g., see the review by Luhmann and Bauer, 1992] allows us to model some of the details of the scavenging process over time. Of course, this presumes that the contemporary loss processes have been dominant since a solar system age of  $\sim 1$  billion years ( $\sim 3.5$  byr ago), and implies that the magnetic field of Mars was not a consideration after that time as suggested by the dynamo models of Schubert and Spohn [1990].

Of the aforementioned processes (nonthermal escape of neutrals due to photochemistry, ion pickup by the solar wind, and sputtering of neutrals by reentrant pickup ions) Zhang et al. [1992a] calculated the oxygen loss rates of the first two for three epochs in the history of the solar system corresponding to solar EUV intensities of 6, 3, and 1 times the present value. According to the solar evolution model of Zahnle and Walker [1982], these values represent solar system ages of  $\sim 1.0$ ,  $2.0$ , and  $4.5$  billion years, respectively. In this note we present the corresponding results for the sputtering process. We show that oxygen sputtering losses are comparable to those from the other mechanisms. However, the accompanying  $CO_2$  losses,

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